UDC 666.1.053.562(047).001.6

THE EFFECT OF THE GAS ATMOSPHERE ON THE PHYSICOCHEMICAL PROCESSES IN FLOAT-GLASS FORMATION (REVIEW)

V. I. Kondrashov,[1] N. A. Frolova,[1] and V. S. Bezlyudnaya[1]

Translated from Steklo i Keramika, No. 6, pp. 13 – 15, June, 2001.

The effect of the gas atmosphere on the physicochemical processes in float-glass production is considered based on the analysis of the patent and scientific literature and the research carried out at the Saratov Institute of Glass. The methods for controlling the physicochemical conditions in the melting tank are described. The possibilities of deliberately modifying the composition and properties of float glass using the effect of the gas medium are demonstrated.

In producing polished glass by the float method, tin melt is used, which is protected from oxidation by a protective nitrogen-hydrogen gas atmosphere (U.S. Patent No. 1564240, Gr. Britain Patent No. 1010914) [1].

The recommended composition of the nitrogen-hydrogen atmosphere for the float process implies the following content of the main components (%): 4 – 15 H_2 and 85 – 96 N_2, and virtually total absence of contaminating impurities. However, practice shows that some impurities, such as oxygen, moisture, carbon monoxide, carbon dioxide, sulfur dioxide, and hydrogen sulfide, as well as gaseous tin oxide and tin(II) sulfide, are inevitably present in the melting tank.

In a well-organized production process, the content of sulfur dioxide in the protective atmosphere and in air used to produce nitrogen through compression and fractional distillation is severely limited and does not exceed 0.0001 vol.%. Therefore, the presence of sulfur in the float tank is due to its release from glass, and the presence of carbon is due to its release from refractory lining. The sulfur dissolves in the tin, and then evaporates from the tin melt in the form of sulfide SnS, which partly reacts with hydrogen in the gas phase. Therefore, the melting-tank atmosphere always contains tin sulfide vapor, which becomes condensed on the cold roof and chillers, and also hydrogen sulfide. Furthermore, sulfur reduced from the glass evaporates from the glass surface in the form of H_2S.

It is impossible to completely exclude the penetration of oxygen and oxygen-bearing compounds into the melting tank, as they inevitably penetrate into the tank, even if it has a high degree of air-tightness, and also penetrate into the protective atmosphere and appear as a result of emissions from the glass. This process is stimulated not only by the temperature and constant renewal of the surface (spreading and stretching of the glass layer) but also by the existence of a partial vacuum with respect to the specified components (O_2, H_2O, CO_2, etc.). As a result, tin is oxidized and evaporates in the form of SnO.

There is a relationship between the main components and impurities in the gas medium and the tin melt. The present study of gaseous components considers hydrogen, oxygen, moisture, gaseous tin (II) oxide and sulfide, hydrogen sulfide, sulfur dioxide, and carbon dioxide.

Let us consider the relationships between the protective atmosphere components and the tin melt:

$$Sn[O] + 2[H] = (Sn) + \{H_2O\}; \quad (1)$$

$$2Sn[O] + Sn[S] = 3(Sn) + \{SO_2\}; \quad (2)$$

$$Sn[S] + 2[H] = (Sn) + \{H_2S\}; \quad (3)$$

$$2Sn[S] = 2(Sn) + \{S_2\}; \quad (4)$$

$$2Sn[O] = 2(Sn) + \{O_2\}; \quad (5)$$

$$Sn[O] = \{SnO\}; \quad (6)$$

$$Sn[S] = \{SnS\}; \quad (7)$$

$$2(Sn) + \{CO_2\} = 2Sn[O] + C. \quad (8)$$

An analysis of the above gas equilibrium relationships is of great significance for the evaluation of the physicochemical factors protecting metallic melt from oxidation.

[1] Saratov Institute of Glass Joint-Stock Company, Saratov, Russia.

Reactions (1) – (3), which yield gaseous moisture {H_2O}, sulfur dioxide {SO_2}, and hydrogen sulfide {H_2S}, are reactions between hydrogen [H], oxygen Sn[O], and sulfur Sn[S] dissolved in tin. Dissolved oxygen and sulfur are not molecules of tin (II) oxide and tin (II) sulfide distributed between the metal atoms. These gases, on being dissolved in tin in the atomic state, produce complexes of different degrees of complexity together with the metal atoms. Reactions (4) and (5) are the processes of disintegration of these complexes with the formation of equilibrium quantities of gaseous oxygen and sulfur.

Independent phases of solid or liquid SnO or SnO_2 and SnS, as well as gaseous {SnO} and {SnS}, exist in tin at equilibrium with saturating concentrations of oxygen and sulfur. Evidently, the gaseous {SnO} and {SnS} are present in the tin melt above the dissolved oxygen and sulfur, which have not reached the saturation level. The equilibrium between gaseous {SnO} and {SnS} and oxygen and sulfur dissolved in tin is represented in reactions (6) and (7).

Reaction (8), reflecting the equilibrium of carbon dioxide {CO_2} and tin {Sn}, is the sum of two reactions:

$$(Sn) + \{CO_2\} = Sn[O] + \{CO\};$$

$$\{CO\} + (Sn) = Sn[O] + (C).$$

The carbon arising as the result of this reaction exists as a condensed phase, since it does not dissolve in tin [2, 3].

The specified reactions show that tin oxide and sulfide are formed in the melting tank and cause defects both on the upper and on the lower surface of the glass (tin oxide adhesion and condensate). There are several methods for solving this problem (USSR Inventor's Certif. Nos. 186659 and 254730; Gr. Britain Patent Nos. 1061811, 1061812, and 1211225). These methods include decreasing the oxygen concentration in tin by correcting the melting-tank gas regime, introduction of additives into the protective atmosphere, development of a protective layer on the surface of molten tin, as well as using a special unit for purification of the protective atmosphere from tin evaporation, and devices for reducing tin oxides on the tin melt surface. Of special interest, in our opinion, is the introduction of special additives into the protective atmosphere of the melting tank

The specialists at the Saratov Institute of Glass identified the relationship between the composition of the gas medium and the activity of oxygen and sulfur in tin, which makes it possible to select a composition of the gas medium which would prevent the formation of tin oxides and sulfides (Fig. 1). Furthermore, the behavior of oxygen in the tank, in which a temperature gradient exists, was analyzed based on the calculation of equilibrium concentrations of oxygen in tin. The following approach was proposed for the selection of the gas-medium composition to prevent the formation of solid oxides on the tin surface: the composition of the protective gas atmosphere should be selected in such a way that an equilibrium oxygen concentration in tin for the higher-temperature regions would not be a saturating concentration for the regions with lower temperatures.

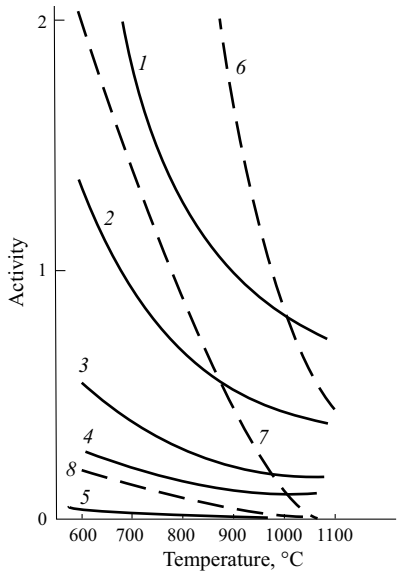

Fig. 1. Activity of oxygen and sulfur in tin: *1*, *2*, *3*, *4*, and *5*) temperature dependence of oxygen activity for a ratio of $p_{H_2O} : p_{H_2}$ equal to 1, 0.5, 0.2, 0.1, and 0.01; *6*, *7*, and *8*) temperature dependence of sulfur activity for a ratio of $p_{H_2S} : p_{H_2}$ equal to 0.01, 0.001, and 0.0001 (p_{H_2O}, p_{H_2S}, and p_{H_2} are partial pressures of moisture, hydrogen sulfide, and hydrogen in a protective atmosphere).

In order to verify these assumptions in practice, one should have access to the current data on the oxygen content in tin. This can be implemented using a special device. Its operating principle is based on measuring the electromotive force generated by an oxygen-concentration battery containing solid electrolyte Zr_2O (0.85) and CaO (0.15). The temperature interval of this device ranges from 600 to 1000°C [4].

According to USSR Inventor's Certif. No. 254730, a protective atmosphere should additionally contain 1.0 – 0.0005 vol.% gaseous halogens or halides to prevent the condensation of metallic tin and its oxides on the glass surface. The chemicals used for this purpose can be chlorine, fluorine, hydrogen fluoride or chloride, ammonium, fluorides and chlorides of various elements highly volatile at the process temperature, or complex compounds containing halides, for example, H_2SiF_6. It is possible to use individual halogens or halides or their mixtures. As the result of the reaction of the latter with tin or tin oxide, tin halides are formed, which have high volatilization. This reaction mainly occurs in the gas phase, since reactions with the participation of liquid tin are thermodynamically less probable and have much lower rates.

The gaseous fluorine, chlorine, and hydrogen fluoride and chloride can be introduced directly in the protective gas. Metal fluorides and chlorides can be introduced in the form of solid powders on a special platform in the hot zone of the

melting tank. The removal of tin halides from the tank occurs together with an excess of protective atmosphere, and oxides are removed mechanically.

Another promising line in increasing the reducing potential of the melting tank is the purification of its protective atmosphere.

It is known that part of the tin compounds are condensed from the gas medium in the form known as microcondensate, i.e., small (1 – 15 μm) particles on the glass surface, which are visible with a microscope or when illuminated against a dark background. Microcondensation is typical for the low-temperature exit part of the melting tank.

All other terms being equal, the condensation of vapors and microcrystalline compounds intensifies as the reducing potential of the melting tank decreases and its contamination with water and oxygen impurities increases. The precipitation of condensate on the upper surface of the glass band can be facilitated by incorrect organization of gas flows inside the melting tank, as a consequence of which a greater part of evaporations in the high-temperature zone of the tank is not removed via the feeder but is transferred to the low-temperature exit zone of the tank.

Thus, Gr. Britain Patent No. 1211225 provides for continuous removal of the protective atmosphere from the high-temperature zone of the float-tank zone and passing it through a purifying system. Such a system can contain an activated carbon filter, gas purifiers, compressors, catalytic chambers, and dryers in various combinations. The purifying system is separated from the tank to allow for continuous removal of impurities without affecting the float-glass production.

The Saratov Institute of Glass has developed devices for purifying protective gas from volatile compounds (SnO, SnS), which are formed over free surface of the tin melt. These devices are installed in the melting tank. Each of them consists of ionizing and receiving electrodes and a collector under them.

Furthermore, certain devices were developed which can actively reduce tin oxides on the tin melt surface. In this case, water vapor is entrained with protective atmosphere flows to the tail end of the tank and removed from it. Such a device consists of a pipeline supplying protective gas and purification devices. The pipeline end is equipped with a nozzle in which ionizing electrodes are placed.

The good prospects for this line of research stems from the possibility of decreasing the volume of protective atmosphere supplied to the melting tanks, which contributes to improving the technical and economical properties of the float process.

Thus, the analysis of patent and technical information indicates that the gas atmosphere has a substantial effect on the physicochemical condition of the float process. The methods for controlling the physicochemical conditions in the melting tank described in the literature, and, in particular, the research carried out at the Saratov Institute of Glass open up vast possibilities for deliberate modification of the composition and properties of float glass by means of control of the gas medium.

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